

FORMATION OF LEWIS ACID SITES IN NaNH_4Y ZEOLITES BY γ IRRADIATION.

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ABSTRACT

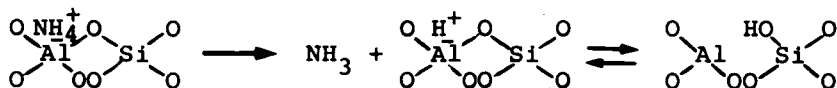
The thermal heating above 500°C and under vacuum (10^{-5} - 10^{-6} torr) of NaNH_4Y zeolite leads to its dehydroxylation with the formation of Lewis acid sites. The same phenomenon occurs upon irradiation with γ rays at room temperature of the same solid preheated to 300°C only.

If the zeolite is preheated above 500°C and irradiated at room temperature, the number of Lewis acid sites formed in the solid is less than when it is simply heated without further irradiation. This decrease is due to the reduction by Compton effect of the strong oxidant sites of this solid keeping the weak sites intact. The electron affinity of the latter increases upon oxygen introduction after irradiation.

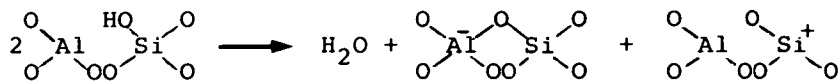
INTRODUCTION

It is well known that certain defects are created in solids under the effect of γ irradiation. This causes different physico-chemical modifications in their properties, some of which are more or less durable (1-3). These defects can play an important role in catalysis specially the electron donor and acceptor centers (4,5).

Authors, using different techniques such as infra-red spectrometry (I.R) (6), electron spin resonance (e.s.r.) (7), thermogravimetry (8,9), X-rays diffraction (9,10), etc., agreed that the above centers are formed during the decomposition of NaNH_4Y zeolite by heating. We generally admit that, on one hand, the decomposition of ammonium ions in zeolites is represented by the following reaction:



and, on the other hand, the dehydroxylation of zeolites is represented as follows:



It was shown that the decomposition of NH_4^+ occurs within the range of 200-300°C and produces Brönsted acid hydroxyl groups. The dehydroxylation occurs above 500°C with the formation of Al electron acceptor sites.

EXPERIMENTAL PART

The starting material was NaY zeolite supplied by "Linde Union Carbide". The Na^+ ions were exchanged by NH_4^+ ions by simple treatment with an ammonium nitrate aqueous solution until the required exchanged levels were reached. The exchanged samples were identified by the number of Na^+ ions remaining in the unit cell. Four samples have been prepared: Na_{56}Y , $\text{Na}_{36,4}(\text{NH}_4)_{19,6}\text{Y}$, $\text{Na}_{16,9}(\text{NH}_4)_{39,1}\text{Y}$ and $\text{Na}_{5,8}(\text{NH}_4)_{50,2}\text{Y}$.

The samples were placed in an e.s.r. tube surmounted by an equipped ampoule of thin glass which is easily broken by a glass hammer. This allows the contact, under vacuum, of anthracene solution with the preheated and irradiated samples (figure 1).

The samples were heated for 15 hours at a given temperature in 160 torr of oxygen and then evacuated (10^{-5} - 10^{-6} torr) at the same temperature for another 20 hours.

The samples were irradiated with doses within a range of 0-20 Mrad at room temperature in a cobalt-60 cell.

After irradiation, the zeolite was poured into a solution of anthracene in benzene (10^{-2}M) prepared in advance. The amount of positive radicals so formed was measured quantitatively by e.s.r. at room temperature using Varian E9 spectrometer. The concentration of the paramagnetic species was measured by comparison with the diphenyl-picryl-hydrazyl (D.P.P.H.) radicals in benzene.

RESULTS AND DISCUSSIONS

When a sample of NaNH_4Y zeolite heated in vacuum at different temperatures and irradiated at room temperature comes into contact with a solution of anthracene in benzene, a dark-yellow coloration is observed due to the formation of positive radicals A^+ after the transfer of an electron from an adsorbed molecule of anthracene to the surface of solid. The e.s.r. spectrum obtained has eleven distinct lines. Such hyperfine structure is attributed to the interaction of an electron with 10 protons of the anthracene molecule. The same e.s.r. spectrum have

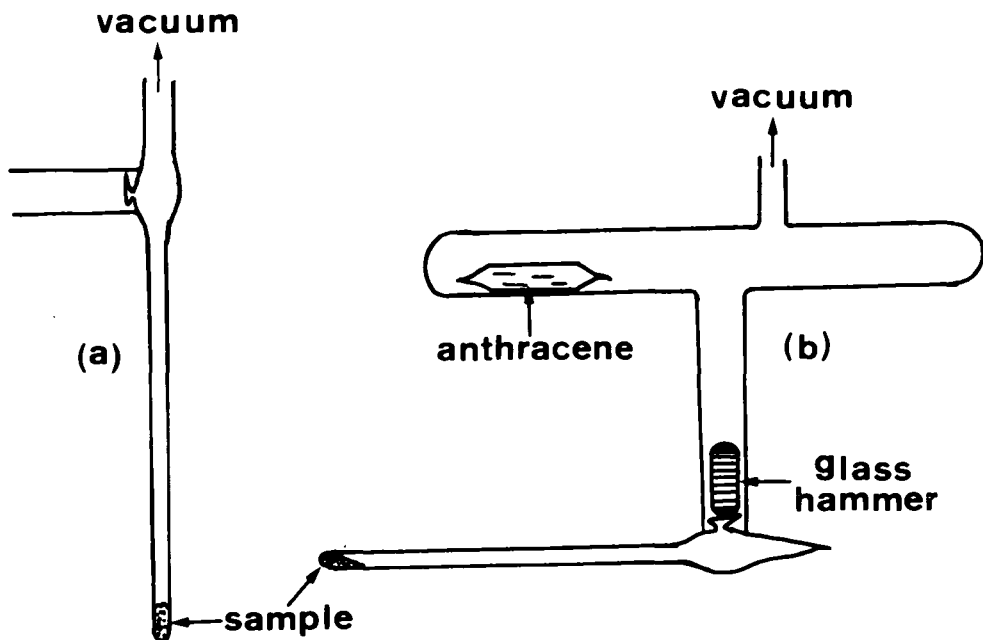


Fig. 1. a) Ampoule used to heat and irradiate the sample under vacuum. b) Ampoule used to introduce the anthracene under vacuum.

been obtained by adsorption of anthracene solution on the non-irradiated zeolite (11).

The curves in figure 2 represent the evolution of the number of positive radicals of anthracene A^+ formed on the irradiated NaNH_4Y zeolite as a function of temperature. We observe that the number of A^+ formed at the irradiated zeolite with a dose of 12 Mrad is different from that at a non-irradiated solid. If the heating temperature is increased, the concentration of A^+ formed on the irradiated samples increases between room temperature and 300°C , remains constant between 300 and 400°C , decreases between 400 - 500°C and doesn't change if the temperature is increased further on.

When we compare these curves with those obtained from the variation in the loss of weight (thermogravimetry) (8), the intensity of OH groups (infra-red) (6) and the length of unit cell crystal (X-rays diffraction) (9) of NaNH_4Y zeolites as a function of temperature, we notice, on the first hand, that the increase in A^+ number formed on the non-irradiated zeolites and, on the other hand, that the decrease in this number on the irradiated solids are within the temperature range at which the dehydroxylation of zeolites occurs. It seems that the acceptor sites of Al are responsible for the formation of A^+ radicals.

In addition, the number of A^+ formed on an irradiated zeolite

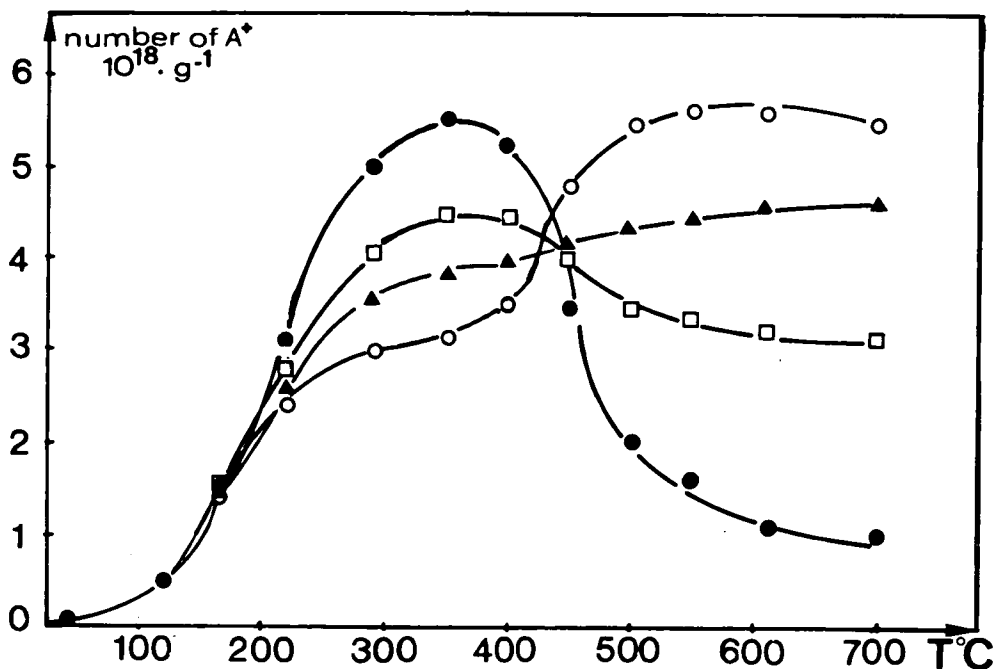


Fig. 2. Evolution of the number of positive radicals of anthracene A^+ formed at the irradiated $Na_{5,8}(NH_4)_{50,2}Y$ zeolite as a function of temperature. ○: 0 Mrad, ▲: 4 Mrad, □: 8 Mrad ●: 12 Mrad.

preheated at a temperature less than $500^\circ C$, is more than the number of A^+ formed on a non-irradiated sample preheated at same temperature but equal to this formed on a non-irradiated zeolite preheated at a temperature above $500^\circ C$.

On the contrary, the A^+ concentration formed on the irradiated zeolite preheated at a temperature above $500^\circ C$ is much lower than this obtained on the non-irradiated zeolite preheated at same temperature.

The increase in the number of electron acceptor sites by γ irradiation at a heating temperature less than $500^\circ C$ may be explained by admitting that the γ rays liberate oxidant sites by dehydroxylation of the solids. The behavior of $Na_{5,8}(NH_4)_{50,2}Y$ zeolite heated at different temperatures and irradiated with doses ranging between 0-20 Mrad have been studied. The number of A^+ formed between 300 and $400^\circ C$ increases with the dose of irradiation and becomes constant above 12 Mrad. This constant is the same as the number of A^+ formed by heating a solid above $500^\circ C$ without irradiation (figure 2).

In order to confirm that irradiation replaces heating in dehydroxylation of zeolite, several $NaNH_4Y$ samples having various ratios

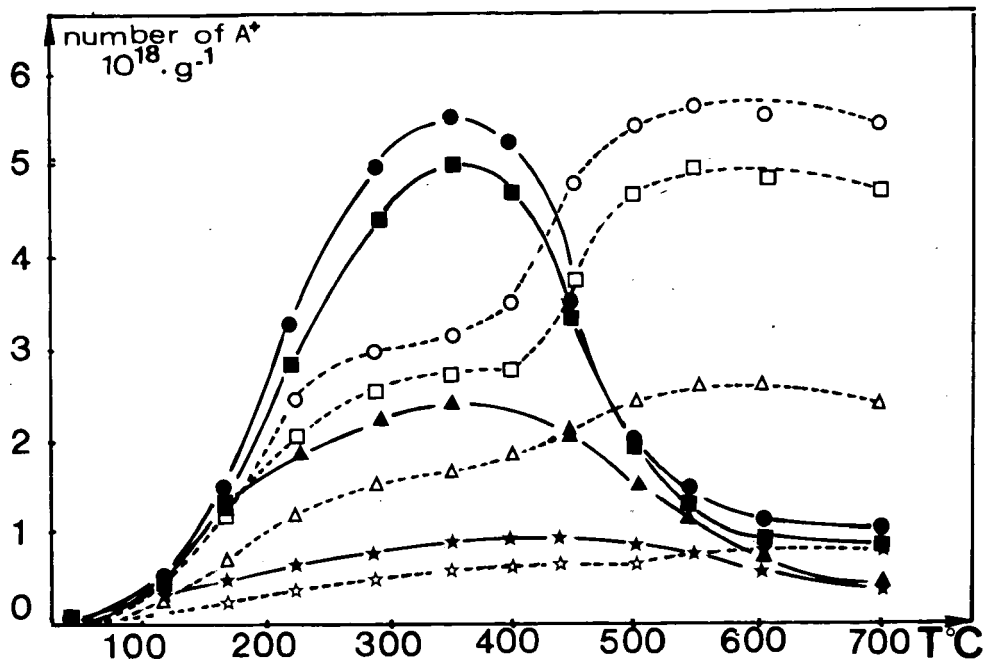


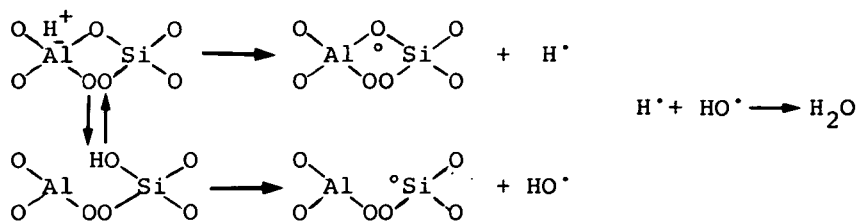
Fig. 3. Evolution of the number of positive radicals of anthracene A^+ formed at the irradiated (—) and non-irradiated (---) $NaNH_4Y$ zeolite as a function of temperature: (☆) $Na_{56}Y$, (▲) $Na_{36,4}(NH_4)_{19,6}Y$, (■) $Na_{16,9}(NH_4)_{39,1}Y$, (○) $Na_{5,8}(NH_4)_{50,2}Y$.

of Na^+/NH_4^+ have been heated at different temperatures and irradiated by 15 Mrad. We notice that the plateaus obtained between 300 and 400°C increase with the number of NH_4^+ in the unit cell of zeolite and are the same as those formed by the solids heated above 500°C but not irradiated (figure 3).

In addition, we have rehydrated, at room temperature, a sample preheated at 300°C and irradiated with a dose of 15 Mrad. Further treatment at 300°C without irradiation, we observed that the number of A^+ radicals was the same as this obtained from a non dehydroxylated sample. The same phenomenon have been observed with a sample heated at 500°C then rehydrated at room temperature with a further treatment at 300°C. These results confirm that zeolites can be dehydroxylated by γ irradiation.

As an evidence for a probable mechanism of the dehydroxylation of zeolites by irradiation, we suggest that the irradiation will form OH radicals and hydrogen atoms which will combine together to form water. The presence of these entities have been proved in our previous work (12). The suggested mechanism for the dehydroxylation is the

following:



The electron acceptor centers obtained in this mechanism have previously been studied and observed by us (13).

The decrease in the electron acceptor centers under the effect of γ irradiation when a sample is heated above 500°C may be due to modifications in texture and structure of the zeolite. We have proved by X-rays analysis that the structure of the sample is not modified by irradiation (14). In addition, the specific area, determined by B.E.T. method, of $\text{Na}_{5,8}(\text{NH}_4)_{50,2}\text{Y}$ heated at different temperatures and irradiated by 15 Mrad is the same as this obtained from a non-irradiated solid (table 1). So, we can suppose that the reduction of acceptor centers by

Table 1

Comparison of specific area of irradiated and non-irradiated $\text{Na}_{5,8}(\text{NH}_4)_{50,2}\text{Y}$ zeolites

Heating temperature °C	300	400	450	500	600	700
Specific area of non-irradiated zeolite m^2/g	707	724	737	698	700	550
Specific area of irradiated zeolite m^2/g	705	713	740	698	703	558

the ejection of an electron by Compton effect during the irradiation.

To prove that the reduced centers are produced by γ irradiation, we put the irradiated and non-irradiated zeolites in contact with excess oxygen after the adsorption of anthracene. We observe in both cases that a sharp increase in the A^+ number will occur principally for the samples heated at high temperature but this number is less in the case of irradiated zeolite (figure 4) specially at the temperature above 500°C.

To interpret the increase in A^+ number in the presence of oxygen, we suggest two possibilities:

i) The A^+ radicals possess a long spin-lattice relaxation time T_1 which presents a saturated e.s.r. signal. Oxygen which has a short T_1

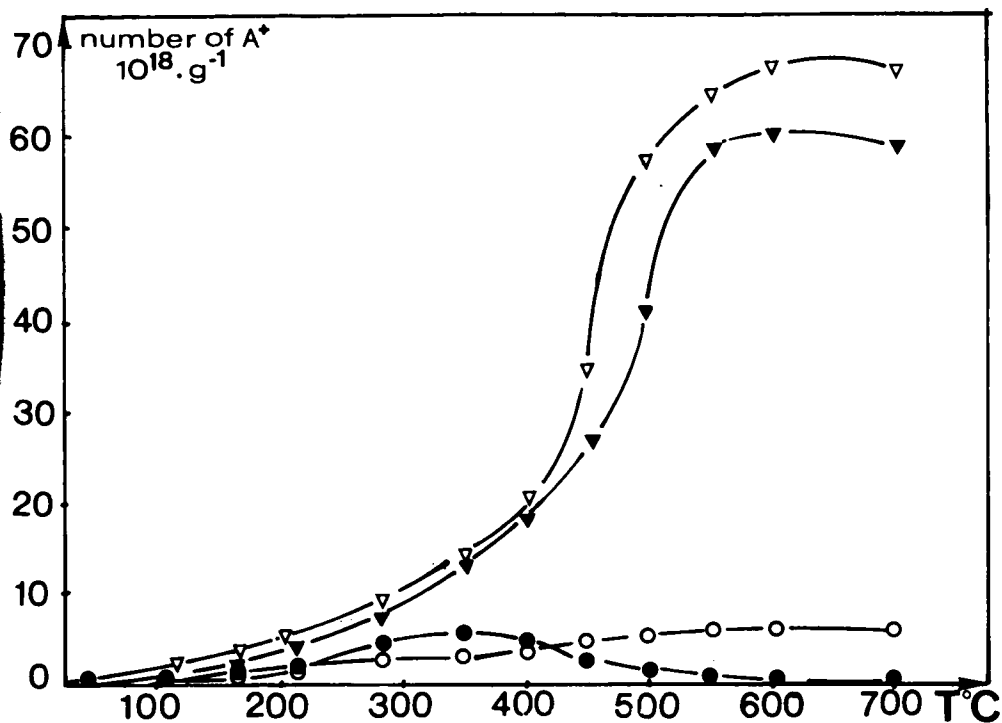


Fig. 4. Evolution of the number of positive radicals of anthracene A^+ formed at the irradiated (●) and non-irradiated (○) $Na_{5,8}(NH_4)_{50,2}Y$ zeolite under vacuum (●) and in presence of oxygen (▼).

is capable of raising the saturation, thus increasing the intensity of the e.s.r. signal. This increase doesn't correspond to the real A^+ number present in the solid.

ii) Oxygen which possesses an electron affinity can play the role of an electron acceptor center. Thus it contributes to the increase in the electron affinity of some weak sites which will cause the formation of new A^+ radicals. Hall and coll (15) showed that the oxygen used in the reaction of charge transfer is strongly adsorbed on the zeolite.

Although, we have recorded the e.s.r. signal at a lower hyper-frequency field to avoid the saturation of signal. It is logical to admit that second possibility is more adequate to interpret the increase in A^+ number in the presence of oxygen.

The difference in the number of A^+ observed on the irradiated and non-irradiated zeolite, after the introduction of oxygen is due to the reduction of strong electron acceptor sites by γ irradiation before oxygen is introduced. The latter is responsible for the increase in

the electron affinity of the weak sites. In the case of the non-irradiated zeolite, the oxygen increases the electron affinity of the weak and strong sites. This explains that the number of A^+ formed on the non-irradiated zeolite is greater than this formed on the irradiated.

CONCLUSION

We conclude from the above study that $NaNH_4Y$ zeolites heated under vacuum, at different temperatures, and irradiated by γ rays, creates weak and strong electron acceptor sites capable of transforming anthracene into a positive radical ion.

The irradiation modifies the number of oxidant sites. It is greater in samples preheated at a temperature below $500^\circ C$ and afterwards irradiated than on the non-irradiated solids. This number is lower on the solids preheated above $500^\circ C$ and then irradiated, than obtained on the non-irradiated zeolites.

The γ rays dehydroxylate the zeolite heated below $500^\circ C$ and reduce the strong oxidant sites formed after dehydroxylation of solid. The weak sites are not modified by γ irradiation but their electron affinity increases in the presence of oxygen then they can ionize anthracene to form the positive radicals.

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